

Final Technical Report  
(September 30, 1995)

ONR CONTRACT INFORMATION

Contract Title: HIGH THERMAL CONDUCTIVITY CARBON/CARBON COMPOSITES

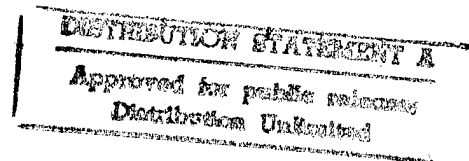
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Contract Number: N00014-92-J-4104 (CU REF:05-5002)

R & T Project Number: C/C 9200---01

ONR Scientific Officer: Steven G. Fishman



## REPORT DOCUMENTATION PAGE

FORM APPROVED  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of the collection of information, including suggestions for reducing the burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302 and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 30 Sep 95	3. REPORT TYPE AND DATES COVERED Final Technical Report 16 Oct 92 - 31 Aug 95	
4. TITLE AND SUBTITLE OF REPORT High Thermal Conductivity Carbon/Carbon Composites			5. FUNDING NUMBERS N00014-92-J-4104	
6. AUTHOR(S) Dr. Dan D. Edie				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Clemson University Box 340909, 123 Earle Hall Chemical Engineering Clemson, SC 29634-0909			8. PERFORMING ORGANIZATION REPORT NUMBER: 05-5002	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research Code 1513:ETF Ballston Tower One 800 North Quincy Street Arlington, VA 22217-5660			10. SPONSORING/MONITORING AGENCY REPORT NUMBER:  19960520 020	
11. SUPPLEMENTARY NOTES:				
12a. DISTRIBUTION AVAILABILITY STATEMENT Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  The objective of this project was to develop a low-cost, high thermal conductivity carbon/carbon composite with a mesophase pitch-based matrix. A low cost, continuous powder coating process was developed which allows the production of a flexible pre-impregnated pitch-based powder. This process was used to produce towpreg from AR mesophase pitch powder and three different carbon fibers: T300 PAN-based fiber, P55 pitch-based fiber, and an experimental high thermal conductivity pitch-based fiber. The thermal conductivities parallel to the fibers of the graphitized T300/AR-120 and P55/AR-120 composites was 80.5 and 135.5 W/m-K, respectively. The ribbon fiber enforced composites exhibited thermal conductivities parallel to the fiber and transverse to the fiber of 145 and 213.5 W/m-K, respectively. This indicates fiber shape can affect matrix properties. A finite element model was developed to predict the thermal conductivity of carbon/carbon composites, both parallel and transverse to the fiber direction, composed of isotropic and anisotropic materials. The model was able to accurately predict the average thermal conductivity of the composites made in this study.				
14. SUBJECT TERMS			15. NUMBER OF PAGES: 15	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT: Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT	

### A. Research Goals

The objective of the project was to develop a low-cost, high thermal conductivity carbon/carbon composite with a mesophase pitch-based matrix. In addition, it was proposed that the project employ a pressure-carbonization technique in order to increase the composite density to approximately 1.5 g/cc, resulting in an increase in both the mechanical and thermal properties of the composites.

### B. Summary

During the course of the study, several significant process improvements were made to facilitate completion of the stated research goals. First, a low-cost, continuous powder coating process has been developed which can produce a flexible pre-impregnated pitch-based towpreg. The flexibility will allow the formation of multidimensional pre-impregnated preforms which can be simply hot pressed into composites. Second, a combination of a pressure-carbonization technique and heat treatment of the mesophase pitch was employed to enhance composite properties by increasing the composite density to 1.5 g/cc - 1.8 g/cc. Next, the effect of specific material variables (such as fiber fraction, fiber structure, matrix structure, fiber/matrix interface and void fraction) was determined using a finite element program. Finally, predictions from the resulting finite element model were compared to measured values. The model was shown to provide adequate predictions under most conditions.

### C. Procedure

Prior to towpreg production, the mesophase pitch powder was prepared to maximize carbon yield. The pitch examined in this study was Mitsubishi AR 2W24, a naphthalene-based mesophase pitch. The anisotropic content of the raw pitch was 100%, and its softening point was 252°C. Table 1 describes the typical Mitsubishi pitch.

The raw AR pitch was heat-treated to remove lower molecular weight components. The low molecular weight components volatilize at 350°C. These volatiles significantly decrease composite properties by disrupting the structure with cracks and pores. The heat treatment involved heat soaking ground pitch at 350°C for two hours. The treatment took place in an inert atmosphere at 0.1 torr. The heat treatment causes the following changes in the pitch: an 80°C increase in softening point, an increased temperature dependence of viscosity (Figure 1), and a 30% increase in carbon yield at 800°C (Figure 2). The heat-treated pitch is labeled AR-120.

Table 1. Chemical and physical properties of a typical Mitsubishi Gas Chemical Company AR mesophase pitch.

Softening Point	251 °C
Anisotropic Content	100%
H/C ratio (atom/atom)	0.61
Specific Gravity	1.26 - 1.30
Fluorine Content	1.7 ppm
Ash Content	4 ppm
Solubility by Soxhlet-extraction	
Heptane Insoluble	98%
Toluene Insoluble	71%
Pyridine Insoluble	49.5%

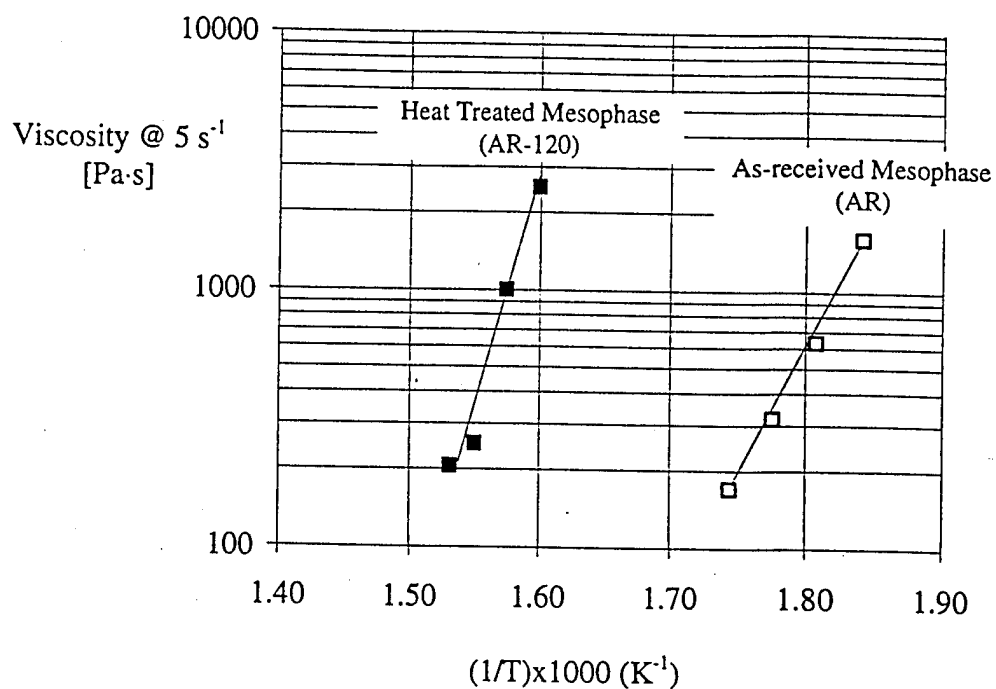


Figure 1. Melt viscosity versus temperature for AR mesophase pitches.

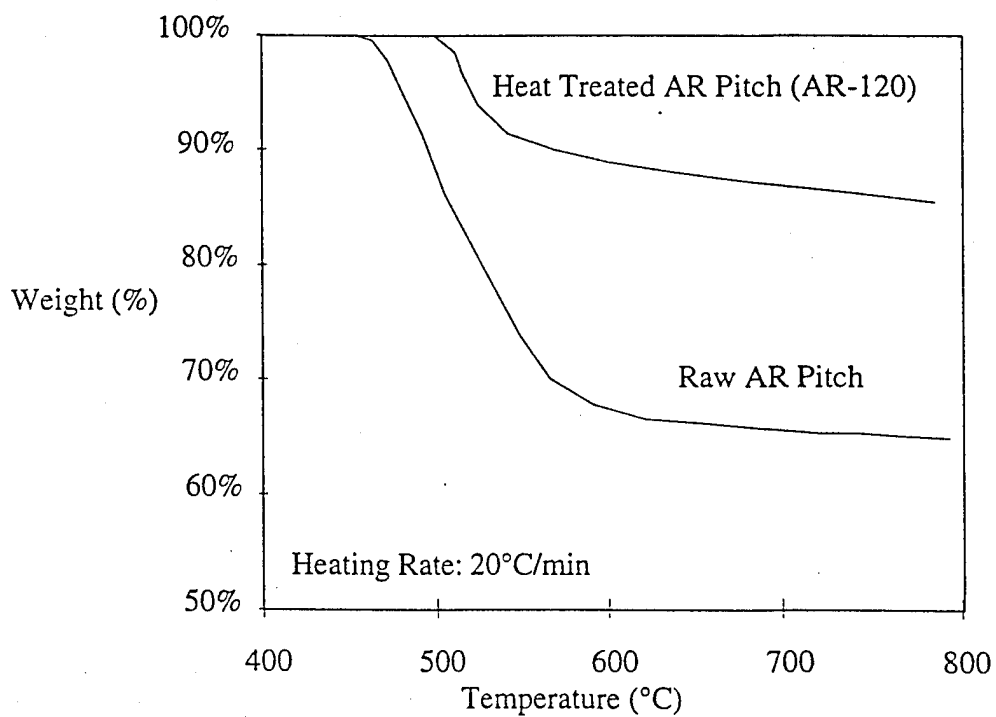


Figure 2. Carbon yield for both the raw AR and the AR-120 mesophase pitches.

The powder coating process (Figure 3) was developed in previous work at Clemson University and is an alternative to the traditional melt impregnation and CVD techniques. This process involves covering a carbon fiber tow with a mesophase pitch powder. The towpreg was directly heat-pressed to form a carbon/carbon composite. The green composites can then be stabilized in the presence of oxygen for 96 hours at 220°C. The stabilization step significantly decreased the occurrence and severity of composite bloating and warping during heat treatment.

After stabilization, the composite was then pressure carbonized to 1100°C in an inert atmosphere. A heating ramp of 0.5 °C/min was used in order to minimize the formation of microcracks and slit pores caused by the thermal expansion mismatch between the fibers and the pitch. The samples then underwent graphitization to 2400°C under a continuous helium purge. Heating and cooling rates of 20°C/min were used.

Some mechanical testing was performed, but the majority of the work involved optical and thermal testing. Cross sections of the composites were examined to determine fiber fraction, fiber structure, matrix structure, fiber/matrix interface, void fraction, and pore location. The thermal diffusivity was measured parallel and perpendicular to the fiber direction using a diffusivity test apparatus at Oak Ridge National Laboratory.

A finite element method was used to model the heat transfer through a carbon/carbon composite. The parameters for the model were experimentally determined and the grid was designed based on results obtained from optical microscopy. Thermal conductivities were calculated for various microscopic sections and stored in a database. Random microscopic sections were assembled to obtain temperature profiles for a carbon/carbon composite.

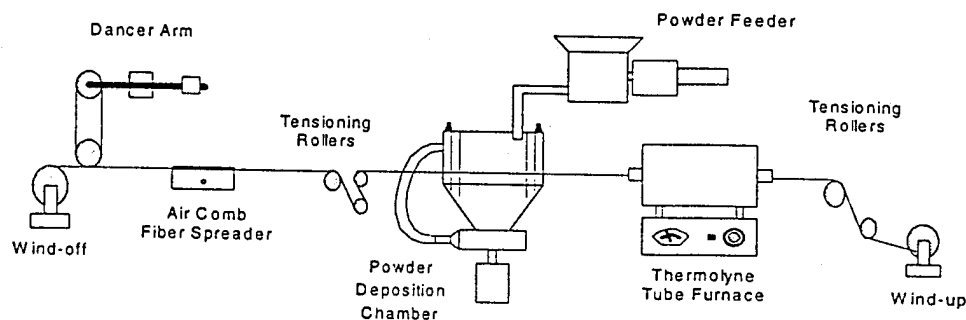


Figure 3. Powder coating method for producing carbon/carbon towpreg.

## B. Significant Results

### **Powder Coating**

A continuous powder coating process was used to produce towpreg from Mitsubishi AR mesophase pitch powder and three different carbon fibers: T300 PAN-based fiber, P55 pitch-based fiber, and an experimental high thermal conductivity pitch-based ribbon fiber. The pitch powder was deposited on individual fibers, rather than on bundles of fibers. As a result, the pitch-based towpreg was very flexible and easy to handle. This flexibility will allow the forming of multidimensional pre-impregnated preforms which can be simply hot-pressed into composites.

## Mechanical Properties

The towpreg then was hot-pressed into unidirectional composites and oxidized at 220°C to a mass gain ranging from 2% to 6%. Carbonization of the oxidized T300/AR-120 composites at 1100°C resulted in an average density of 1.54 g/cc (with an average fiber fraction of 56%). However, graphitization at 2400°C increased the average density to 1.69 g/cc (Figure 4). The porosities ranged from 4% to 25% at both heat treatment temperatures, a significant improvement over the 30% to 60% porosities (Figure 5) for composites previously formed from T300 fibers and unstabilized, raw AR mesophase pitch. By comparison, most of the commercial composites produced for the aerospace industry have porosities ranging from 4 to 25%. However, nearly all of these composites have undergone several densification cycles. Thus, by comparison, the specimens made in the present research are excellent.

The carbonized P55/AR-120 composites had an average density of 1.57 g/cc at an average fiber fraction of 56%, very similar to the T300/AR-120 composites. However, the T300/AR-120 composites, the densities of this variety of composites did not change significantly upon graphitization at 2400°C. At both heat treatment temperatures, the porosities of the P55/AR-120 composites ranged from 12% to 27%.

It was observed that the PAN-based fibers developed a strong fiber/matrix bond and the pitch-based fibers developed a weak fiber/matrix bond. This resulted in high flexural strengths in the graphitized composites reinforced with the T300 fibers (841 MPa) and low flexural strengths in the graphitized composites reinforced with the P55 fibers (196 MPa). The results are summarized in Table 2.

Table 2. Mechanical Properties of carbon/carbon composites formed from mesophase pitch-based towpreg and two different carbon fibers.

Composite	Final Heat Treatment Temp. [°C]	Fiber Tensile Modulus [GPa]	Fiber Tensile Strength [MPa]	Composite Flexural Modulus [GPa]	Composite Flexural Strength [MPa]	Failure Mode
T300/AR-120	1100	221	3.0	129±30	691±48	Non-catastrophic Tensile
	2400	302	1.8	196±34	841	Catastrophic Tensile
P55/AR-120	1100	403	1.8	147±50	162±62	Buckling & Compression
	2400	~500	2.1	216±61	198±8	Buckling & Compression

## Optical Evaluation

It was found that during consolidation the ribbon fibers oriented normal to the pressing direction (Figure 6), resulting in significant development of structure in the matrix in this direction. This resulted in unique thermal properties of carbon/carbon composites reinforced with ribbon fibers.

Cross-polarized microscopy was used to confirm the formation of a sheath-like structure in a mesophase pitch matrix around round fibers. Due to the small domain size, this technique was unable to confirm the expected fold-sharpening (Figure 7) that occurs during graphitization. Microscopy was also used to determine the extent of formation and location of microcracks formed during heat treatment.

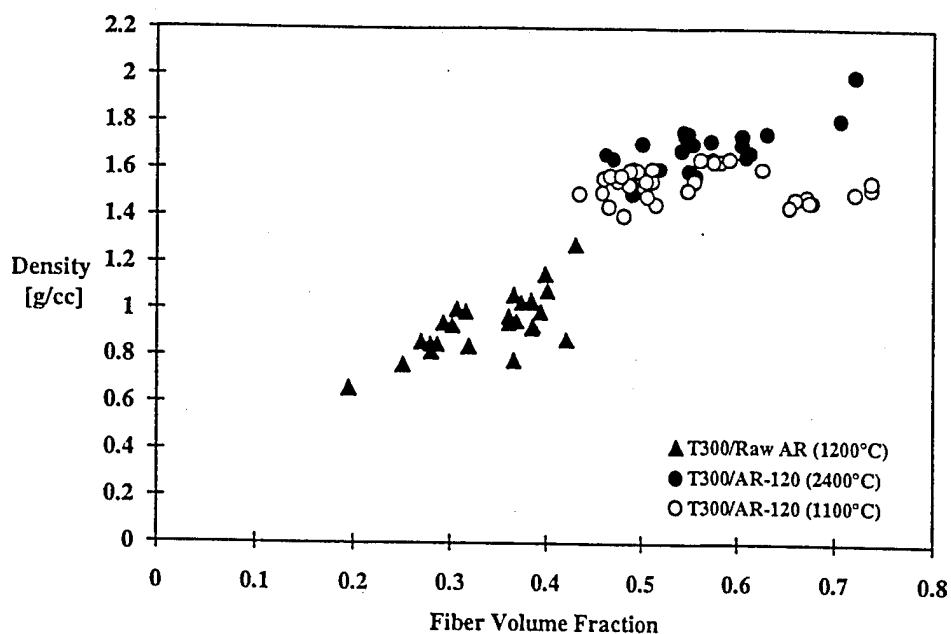


Figure 4. Density versus fiber fraction for carbonized and graphitized composites made from T300 fibers and mesophase pitch.

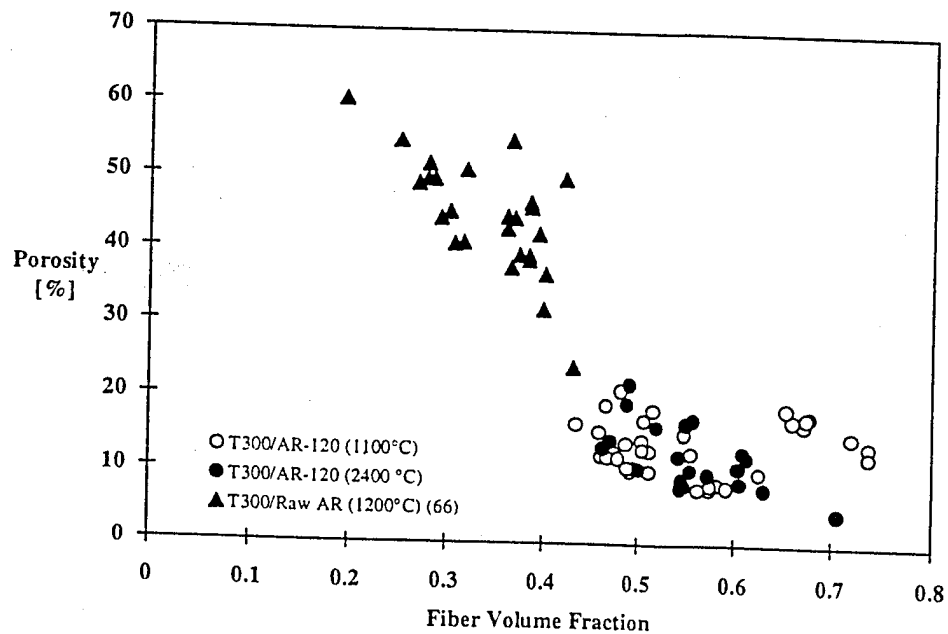


Figure 5. Porosity versus the fiber fraction for carbonized and graphitized composites made from T300 fibers and mesophase pitch.

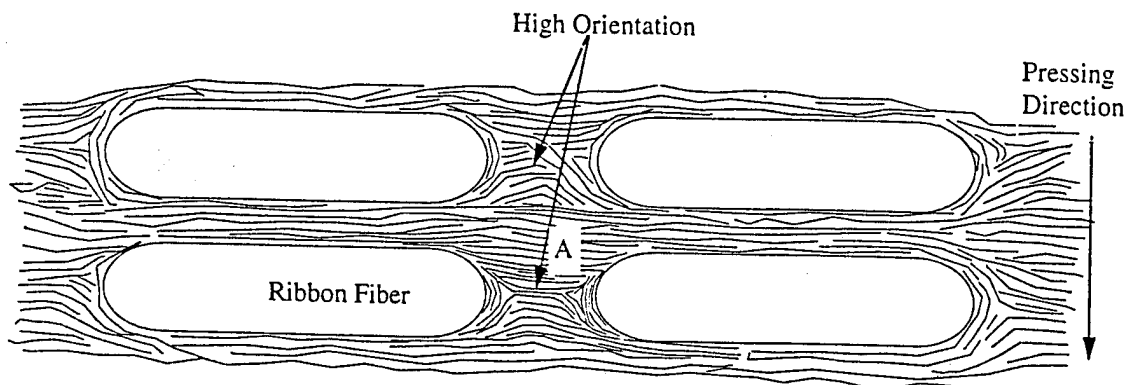


Figure 6. Illustration of matrix orientation in ribbon fiber composites.

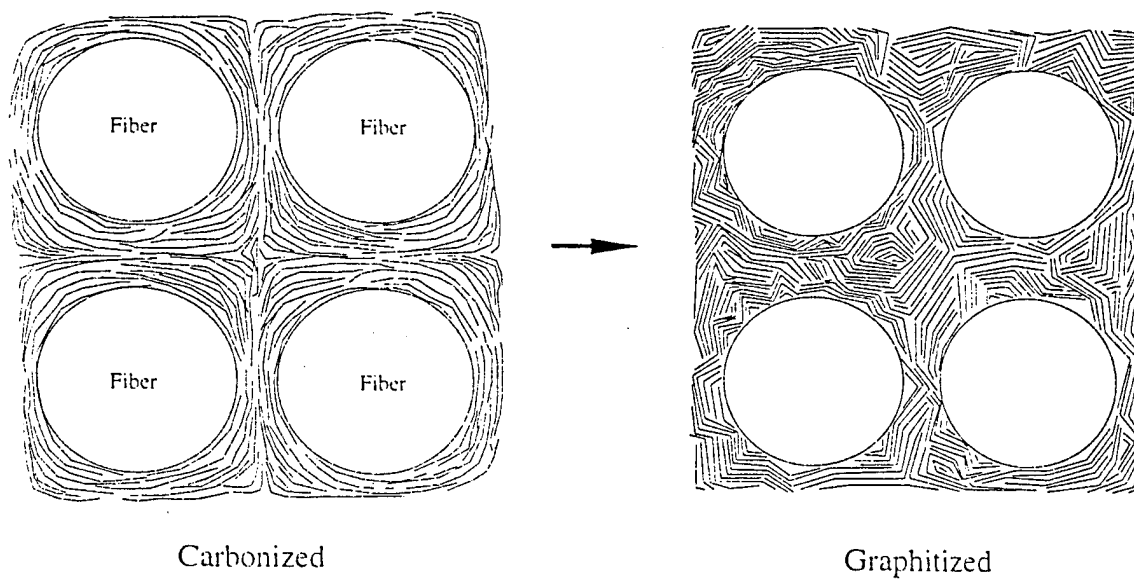


Figure 7. Illustration of fold-sharpening that occurs during graphitization.



### Thermal Conductivity

The thermal conductivity (parallel to the fibers) of the graphitized T300/AR-120 and P55/AR-120 composites was 80.5 and 135.5 W/m-K, respectively. These results, along with x-ray analysis, indicated a significant development of preferred crystalline order (parallel to fibers) upon graphitization at 2400°C. The composites reinforced with ribbon fibers exhibited 3-D anisotropy, with a thermal conductivity (transverse to the fibers) of 213.5 W/m-K, higher than that parallel to the fibers (145 W/m-K). These results are summarized in Table 3 and indicate that fiber shape can affect matrix properties in carbon/carbon composites.

Table 3. Thermal properties of carbon/carbon composites formed from mesophase pitch-based towpreg and three different carbon fibers.

Composite	Fiber Thermal Conductivity [W/m-K]	Final Heat Treatment Temperature [°C]	Parallel Thermal Conductivity [W/m-K]	Transverse Thermal Conductivity [W/m-K]
T300/AR-120	8.5	1100	4.86 ± 0.21	---
	76	2400	80.5 ± 2.7	6.86 ± 1.44
P55/AR-120	98	1100	70.8 ± 3.7	2.40 ± 0.40
	196	2400	135.5 ± 4.3	---
Type I ribbon/AR-120	236	2400	148.2	213.5

### Finite Element Model

A finite element model was developed to predict the thermal conductivity of carbon/carbon composites, both parallel and transverse to the fibers. This model accounts not only for the anisotropic nature of the fibers and matrix, but also for random porosity and different types of fiber/matrix bonding (Figure 8). The model was able to accurately predict the average thermal conductivity of the composites produced in this study. Figure 9 shows graphically the agreement between predicted and measured thermal conductivity for one set of composites. Other composites showed similar agreement. The model successfully predicted the thermal conductivity parallel to the fiber axis for P55 and ribbon fiber composites. The model also predicted the thermal conductivity perpendicular to the fibers for P55 pitch-based fiber composites, but significantly underestimated the conductivity of ribbon fiber composites.

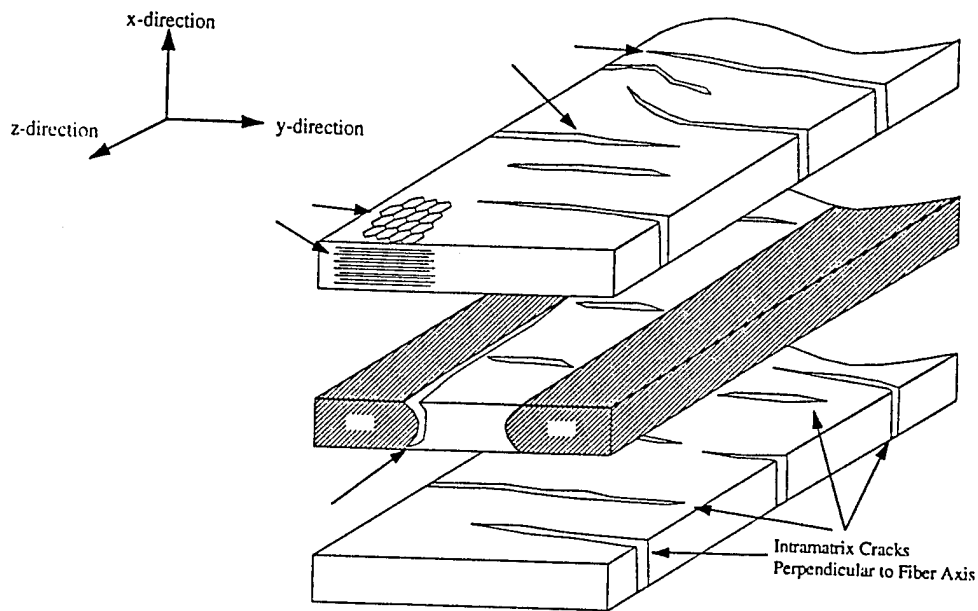


Figure 8. Exaggerated illustration of intramatrix cracking and fiber matrix debonding both parallel and perpendicular to the fiber axis in a ribbon fiber composite.

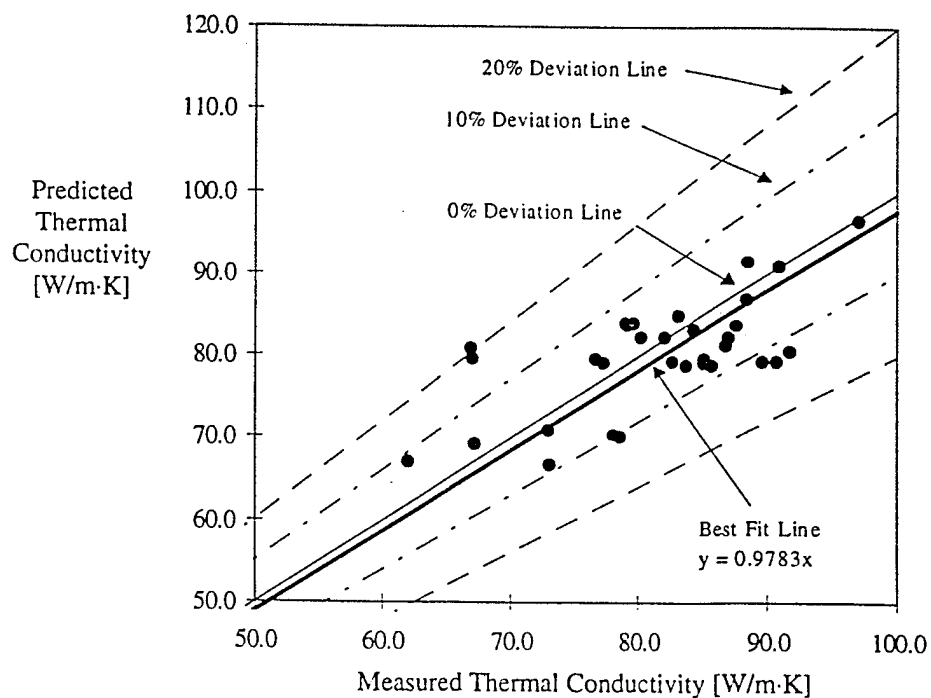


Figure 9. Plot of predicted versus measured thermal conductivity, parallel to the fibers, of individual T300/AR-120 composites heat treated to 2400°C.

### C. Final Recommendations

1. Ribbon fiber and heat-treated mesophase pitch should be used to produce high thermal conductivity carbon/carbon composites.
2. The towpreg fabrication method can be used to widen the processing window to include alternative pitches, which may form better composites in less time.
3. The finite element model produced for this study can be used to study the effect of specific material characteristics, such as fiber texture and fiber/matrix bonding, on the composite thermal conductivity.

### D. References

All figures and tables can be found in the following dissertation: *Heat Transfer in Carbon/Carbon Composite Materials*. J.W. Klett. Clemson University, 1994. Portions of the text were also taken from the dissertation.

D. List of Publications/Reports/Presentations During Grant Period

1. Papers Published in Refereed Journals

"Flexible Towpreg for the Fabrication of High Thermal Conductivity Composites," J. W. Klett and D. D. Edie, Carbon, in press.

2. Non-Refereed Publications and Published Technical Reports

"Modeling the Effects of Porosity and Fiber Structure on the Thermal Conductivity of Carbon/Carbon Composites Using the Finite Element Method," J. W. Klett, D. D. Edie, and V. J. Ervin, Carbon '94, Proceedings of the 6th International Conference on Carbon, Granada, Spain, July 3-8, 1994, pp. 688-689.

"Flexible Towpreg for Carbon/Carbon Composites," J. W. Klett and D. D. Edie, Proceedings of the 21st Biennial Conference on Carbon, Buffalo, NY, June 13-18, 1993, pp. 48-49.

3. Presentations

a. Invited

"High Thermal Conductivity Carbon/Carbon Composites," American Carbon Society Workshop.

b. Contributed

(See item 2 above.)

4. Books (and sections thereof)

Enclosure (2)

E. List of Honors/Awards During Grant Period

<u>Name of Person Receiving Award</u>	<u>Recipient's Institution</u>	<u>Name, Sponsor and Purpose of Award</u>
Dan D. Edie	Clemson University	1993 George Graffin Lectureship, American Carbon Society, for contributions to the field of carbon science and engineering
Dan D. Edie	Clemson University	Elected to the Executive Council of the American Carbon Society

F. Participants in EPSCOR Grant

James W. Klett, completed Ph.D. in Chemical Engineering and graduated from Clemson in December, 1994.

Richard M. Dayrit, minority student currently enrolled as an M. S. student in Chemical Engineering.

Both of the above are U. S. citizens

G. Other Sponsored Research During Grant Period

This Grant

"High Thermal Conductivity Carbon/Carbon Composites," Office of Naval Research, \$95,100, 0% of time, (1992-1995) \$95,100

Other Grants

"High Thermal Conductivity Fibers," Sponsored by the Great Lakes Composite Consortium, \$220,000/yr, 30% of time, 1/1/92 to 12/31/95.

"High Thermal Conductivity Fibers from PBO," Sponsored by ONR, 0% of time, \$31,000/yr, 7/31/94 to 8/1/97.

"Graphitization Kinetics of PBO," Sponsored by Dow Chemical, 5% of time, \$35,000/yr, 4/1/93 to 9/30/94.

"Production of Carbon Monofilament," Sponsored by MSNW, \$84,300/yr, 5% of time, 1/1/93 to 5/20/94.

"Production of Carbon Monofilament- Phase II," Sponsored by MSNW, \$150,000/yr, 5% of time, 3/3/95 to 5/3/96.

"Supercritical Extraction for High Thermal Conductivity Fibers - Equipment Grant," Sponsored by DoD, \$130,000/yr, 0% of time, 9/16/93 to 8/31/94.

"Supercritical Extraction for High Thermal Conductivity Fibers," Sponsored by DEPSCoR, \$100,000/yr, 15% of time, 9/1/94 to 8/31/97.

"Engineering Fibers and the Micromechanics of Their Composites," Sponsored by NSF, \$95,000/yr, 17% of time, 7/1/91 to 6/31/94.

H. Summary for Grant Period

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/PARTICIPANTS  
(Number Only)

	<u>ONR</u>	<u>non ONR</u>
a. Number of Papers Submitted to Referred Journal but not yet published:	_____	<u>1</u>
b. Number of Papers Published in Refereed Journals:	_____	_____
c. Number of Books or Chapters Submitted but not yet Published:	_____	_____
d. Number of Books or Chapters Published:	_____	_____
e. Number of Printed Technical Reports & Non-Referred Papers:	_____	<u>2</u>
f. Number of Patents Filed:	_____	_____
g. Number of Patents Granted:	_____	<u>1</u>
h. Number of Invited Presentations at Workshops or Prof. Society Meetings:	_____	<u>1</u>
i. Number of Contributed Presentations at Workshops or Prof. Society Meetings:	_____	<u>2</u>
j. Honors/Awards/Prizes for Contract/Grant Employees: (selected list attached)	_____	<u>1</u>
k. Number of Graduate Students and Post-Docs Supported at least 25% this year on contract grant:	_____	<u>2</u>

Grad Students:	TOTAL	_____	<u>2</u>
	Female	_____	_____
	Minority	_____	<u>1</u>
Post Doc:	TOTAL	_____	_____
	Female	_____	_____
	Minority	_____	_____

Enclosure (4)

1. Number of Female or Minority PIs or CO-PIs

New Female	_____	_____
Continuing Female	_____	_____
New Minority	_____	_____
Continuing Minority	_____	_____

Enclosure (4) contd.